

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 January 2002 (31.01.2002)

PCT

(10) International Publication Number  
WO 02/09161 A2

- (51) International Patent Classification<sup>7</sup>: H01L 21/00 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (21) International Application Number: PCT/US01/23047
- (22) International Filing Date: 23 July 2001 (23.07.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/621,928 24 July 2000 (24.07.2000) US
- (71) Applicant: SAINT-GOBAIN CERAMICS & PLASTICS, INC. [US/US]; 1 New Bond Street, Worcester, MA 01615-0137 (US).
- (72) Inventor: HAERLE, Andrew, G.; 10 Donald Street, Northboro, MA 01532 (US).
- (74) Agent: MIRABITO, A., Jason; Mintz, Levin, Cohn, Ferris, Glovsky and Popeo P.C., One Financial Center, Boston, MA 02111 (US).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
--- without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/09161 A2

(54) Title: PROCESS FOR CLEANING CERAMIC ARTICLES

(57) Abstract: A method for cleaning ceramic workpieces such as SiC boats used in semiconductor fabrication is disclosed. The method comprises washing a virgin or used ceramic workpiece with a chemical stripping agent and then using a pelletized CO<sub>2</sub> cleaning process on the acid washed component. The inventive method has been found to produce a workpiece having a very low level of metallic and particulate contaminants on its surface.

## PROCESS FOR CLEANING CERAMIC ARTICLES

### Field of the Invention

- 5 The present invention relates to methods for cleaning ceramic articles. More particularly, the present invention relates to method for removing both particle impurities and chemical impurities from ceramic articles used in the manufacture of semiconductor devices.

### Background of the Invention

- 10 The manufacture of semiconductor devices typically requires subjecting the surface of a silicon wafer to high temperature processes such as diffusion, oxidation and deposition. In deposition processes, dielectric materials such as polycrystalline silicon, silicon nitride and silicon dioxide are deposited on the surface of the wafer. In diffusion processes, materials are diffused into the body of the silicon wafer. In oxidation processes, the surface of the
- 15 wafer is oxidized to form a thin silica layer. Each of these processes typically involves placing the wafers to be processed in a holder, often called a "boat". The boat is typically formed of a ceramic material and is configured to hold the wafer in either a horizontal or a vertical orientation. Once loaded with wafers to be processed, the boat is placed in an electrically-heated furnace or process tube, and then the environment inside the tube is altered
- 20 to provide various atmospheres having temperatures typically ranging from 250 °C to over 1200 °C.

- Another common semiconductor process is etching. After a photolithographic pattern is deposited on the surface of a silicon wafer, the wafer is loaded into an etcher. The etcher,
- 25 whose components are typically made of a ceramic material, uses a plasma etching process to remove the materials deposited on the wafer surface which are not protected by a photolithographic pattern. The typical etching process removes oxides, metals and/or polymers from the wafer surface.

Although each of the processes described above successfully develops the surface of the silicon wafer into a useable product, they also eventually contaminate the surfaces of the supporting equipment as well. For example, a nitride deposition process will leave a coating of silicon nitride upon not only the wafer, but also upon the surface of the boat which  
5 supported the wafer during the deposition process. When this coating becomes too thick, it tends to flake and contaminate nearby wafers with particles.

In an etching process, the deliberate removal of various layers of material from the wafer-in-process can cause contaminant particles such as silica, nitrides, and alumina to be deposited  
10 on the surface of etcher components. Since contaminants adversely affect the processing of future wafers to be processed by these components, contaminant particles must be carefully cleaned from the surfaces of these components. Because of the decreasing line widths of silicon wafers, it has become increasingly important to remove more sub-micron particles from the surface of these components, more particularly sub-micron particles having a width  
15 of no more than 0.7 microns.

Several methods for cleaning used ceramic boats are known in the prior art. In one method, a used component which is coated with a deposited material such as silicon nitride, polysilicon or silica undergoes a two-step cleaning process whereby the component is first exposed to a  
20 stream of hard pellets, such as silicon carbide pellets, in a process akin to sand-blasting, and then to a stream of frozen carbon dioxide (CO<sub>2</sub>) pellets. The first step, termed preliminary cleaning, successfully strips deposited material from the component surface, leaving behind some debris particles on the order of one micron. In the second step, termed primary cleaning, the frozen CO<sub>2</sub> pellets are believed to cause the micro-sized debris particles to  
25 freeze, thereby becoming brittle, and then break, thereby allowing them to be easily flushed from the surface.

Preliminary cleaning is ordinarily carried out either by impinging or "blasting" glass, aluminum oxide, silicon carbide, titanium oxide, walnut shell particles, or other hard beads

WO 02/09161

PCT/US01/23047

against the part being cleaned. The beads are typically carried in a pressurized stream of air or other gas. The beads can be spherical, granular, or any other desired shape and dimension. One commonly used bead material is 98% black SiC grit. The pressure under which the beads are directed to the surface depends on the composition of the part being cleaned. When a ceramic part is to be cleaned, the beads typically are applied in a gas at a pressure in the range of about 20-35 psi. Once completed, the bead blasting, preliminary cleaning, step is followed by a CO<sub>2</sub> cleaning process. CO<sub>2</sub> cleaning processes have been described in the patent literature. See, for example, U.S. Patent No. 4,707,951, entitled "Installation for the Projection of Particles of Dry Ice", and U.S. Patent No. 6,004,400, entitled "Carbon Dioxide Cleaning Process".

In another method of cleaning a used boat which is coated with deposition layers, one manufacturer recommends subjecting the used boat to an acid treatment, preferably using a strong acid such as HF, followed by baking. This HF treatment removes the deposited layer of material.

The cleanliness of virgin semiconductor processing equipment has also been a concern in the art. However, for a virgin part, the concern has typically been metallic, rather than particulate, contamination. In one conventional method of manufacturing SiC diffusion components, the virgin SiC diffusion components are subjected to a weak acid and then baked. This process serves to remove some metallic contaminants and fingerprints from the part being cleaned.

In another conventional method of insuring the cleanliness of virgin components, the component is subjected to a strong acid such as HF prior to installing it in a furnace. Similarly, hot HCl cleaning has been used in connection with semiconductor diffusion components. For example, in UK Patent Application No. GB 2,130,192, the investigators disclose a manufacturing step of subjecting a virgin SiC component to hot HCl treatments prior to use in a semiconductor furnace.

In some cases, HF treatment by itself has been considered sufficient for cleaning both virgin boats (to reduce metallic contamination) and used boats (to chemically strip coatings deposited during semiconductor processing). That notwithstanding, the use of HF alone fails  
5 to remove problematic debris particles that may still be present after such treatment.

In sum, conventional methods of providing a clean virgin semiconductor component involve acid cleaning to remove metallic contamination, while conventional methods of cleaning used components involve either i) a two-step process of mechanical stripping of deposited coats  
10 via bead blasting followed by CO<sub>2</sub> cleaning to remove small debris particles, or ii) hot strong acid cleaning to remove a coat of deposited material.

#### Summary of the Invention

The fabrication of semiconductor devices requires the use of process components having a  
15 high level of surface purity, whether those components are new or reconditioned. In certain workpieces, such as ceramic boats used to position and maintain semiconductor wafers during processing, the long depth and narrow spacing of the wafer-retaining slots define a boat geometry with a contoured surface having an aspect ratio that prevents bead blasting from sufficiently stripping coatings from the deeper portions of these slots. In particular, aspect  
20 ratios, (i.e., the ratio of slot depth to slot width), of greater than about 4:1 are typically beyond the ability of conventional cleaning methods. The present invention presents a method for overcoming this and other shortcomings by providing a process in which the inorganic surface of semiconductor fabrication components is cleaned by chemical stripping followed by CO<sub>2</sub> cleaning.

25

In one embodiment, the chemical stripping is carried out using a solvent containing a strong acid. In a more preferred embodiment, the chemical stripping is carried out using a solvent having at least 1 v/o of an acid selected from the group consisting of HF, acids having a pKa of less than about one, and mixtures thereof. As used herein, "v/o" represents a volume

WO 02/09161

PCT/US01/23047

percent, and "strong acid" represents a solution having at least 1 v/o of an acid having a pKa of less than about one.

Alternatively, chemical stripping may be carried out using any of a wide variety of acids. For example, in one embodiment, chemical stripping is achieved using chlorinated acids. In particular, a chlorinated acid such as HCl may be applied to the surface to be cleaned prior to the CO<sub>2</sub> cleaning step mentioned above. While HCl is desirable due to its high level of dissociation, other acid chlorides, including but not limited to chloroacetic acid, chloropropanic acid and chlorobenzoic acid may be used as well. Use of such acids at elevated temperatures, i.e., about 85°C and above, although not required, will result in improved surface purity.

Of course, the invention is not intended to be limited to chlorinated acids or halogenated acids. Rather, the invention contemplates the use of virtually any acid that is capable of stripping contaminants from the substrate surface. While not a requirement, employing such acids at the elevated temperatures described above is believed to result in improved surface purity.

In yet another embodiment, liquid acid treatment may be replaced by gas-phase chemical stripping agents. For example, prior to the CO<sub>2</sub> cleaning step, surfaces to be cleaned may be treated with a halogen gas or a gas containing halogenated compounds. Thus, the chemical stripping step may be carried out by exposing the surface to gas phase chlorine, fluorine, bromine, iodine, etc., or it may be exposed to a gas-phase chlorinated compound such as SiCl<sub>4</sub>. Gas-phase halogenated organic compounds may be used as well. These include, but are not limited to 1,1,1-trichloroethane (TCA) and 1,2-trans-dichloroethylene (DCE).

In still another embodiment, the use of supercritical fluids as chemical stripping agents is contemplated as well. Supercritical fluids are dense gasses that are maintained at temperatures above their critical temperature (i.e., the temperature above which the gas can no

WO 02/09161

PCT/US01/23047

longer be liquified by pressure). Because supercritical fluids are less viscous and diffuse more rapidly than liquids, they are expected to offer excellent results in chemical stripping applications.

- 5 The CO<sub>2</sub> cleaning step employs particles of dry ice which are projected against the surface being cleaned. The combination of the chemical stripping and the CO<sub>2</sub> cleaning step has been found to successfully remove both particulate and metallic contaminants from the surface of the workpiece.
- 10 Workpieces cleaned using the inventive process have been found to have a surface contaminant particle density of no more than about 0.4 particles, and preferably no more than about 0.2 particles, larger than about 0.3  $\mu$ m per square centimeter. Such workpieces have also been found to have a surface metallic contaminant concentration of no more than about 600 ppm, as measured by SIMS at a depth of about 10 nm. Of the surface metallic
- 15 contamination, no more than about 400 ppm of metal contaminants other than alkaline and alkaline earth metals, and no more than about 225 ppm of iron, (as measured by SIMS at a depth of about 10 nm), remain following application of the inventive cleaning process to typical workpieces.
- 20 One aspect of the present invention is based upon the recognition that problematic debris particles may still be present after chemical stripping, and that CO<sub>2</sub> cleaning steps, while removing particulate contaminants, are unable to remove non-particulate surface metallic contaminants. To date, the art has lacked any suggestion of the present invention which employs chemical stripping to remove surface metallics followed by a CO<sub>2</sub> cleaning step to
- 25 remove any remaining debris particles. Combining a CO<sub>2</sub> cleaning step with chemical stripping is unique in that CO<sub>2</sub> cleaning has traditionally been used only after a used workpiece underwent mechanical stripping which produced debris particles.

In another embodiment of the present invention, methods other than the CO<sub>2</sub> cleaning step may be used to remove particulate debris from the workpiece surface. For example, cleaning may be achieved using sonic energy instead of or in addition to the CO<sub>2</sub> cleaning step. The sonic energy may be applied as ultrasonic or megasonic energy. Megasonic cleaning is related to ultrasonic cleaning in that it uses sound waves in the cleaning process, however, unlike the frequencies employed in ultrasonic cleaning, (approximately 50-250 kHz), megasonic cleaning methods employ frequencies in the range of approximately 700-1000 kHz.

10

The present invention also relates to workpieces, such as ceramic boats used in semiconductor processing, that have been cleaned using the process of the present invention. The resulting workpieces are unique in that their level of metallic and particulate surface contamination is significantly below that which has previously been obtainable using processes known to those skilled in the art.

15

#### Detailed Description of the Invention

The present invention provides a process for providing ceramic workpieces, such as ceramic boats used in semiconductor fabrication with a lower level of metallic and particulate surface contamination than has previously been available. Specifically, whereas it is known in the art to use acid cleaning, and whereas it is also known in the art to use bead-blast cleaning in combination with CO<sub>2</sub> cleaning, to-date, there has been no suggestion in the art to combine a chemical stripping step with a CO<sub>2</sub> cleaning step for cleaning either virgin or used, coated ceramic workpieces. The recognition that a chemical stripping step can be combined with a CO<sub>2</sub> cleaning step yields a cleaning process that is well-suited for use with both virgin and used, coated workpieces.

20

25

As noted above, use of the inventive process has provided workpieces having a surface contaminant particle density of no more than about 0.4 particles larger than about 0.3  $\mu\text{m}$  per



WO 02/09161

PCT/US01/23047

square centimeter, and a surface metallic contaminant concentration of no more than about 600 ppm, as measured by SIMS at a depth of about 10 nm.

Traditionally, upon receiving a virgin workpiece such as a ceramic boat from a manufacturer,  
5 the user would subject the workpiece to an acid cleaning process in order to remove any metallic contaminants that may have deposited on the workpiece during manufacture, packaging, shipping, etc. In some instances, used, coated workpieces would be cleaned by chemical stripping using a strong acid. As with the virgin workpieces, the acid cleaning provided a satisfactory means for removing metallic contaminants from the surface of the  
10 workpiece.

Although chemical stripping provides a surface having metallic contaminants lowered to satisfactory levels, the process fails to provide a surface having a sufficiently low level of particulate contamination. In fact, some evidence exists that the chemical stripping step  
15 actually contributes to particulate contamination. Without wishing to be tied to any particular theory, in cleaning a workpiece such as a used ceramic boat, workpieces cleaned using chemical stripping to remove a coating still have a high level of particulate contamination because the stripping process leaves particulate contaminants on the ceramic surface.

20 Furthermore, particulate contamination does not result solely from the chemical stripping process and post-processing steps. Rather, in the case of virgin workpieces, it is believed that machining the component, such as an SiC boat, produces particles which deposit upon the surface of the component. Of course, particles also may deposit upon a virgin component because of exposure of such components to non-clean-room environments. It should be noted  
25 that, in the case of either virgin or used components, and pre-processing, processing or post-processing steps, many mechanisms for the formation of particles on the workpiece may exist, and the present invention is not intended to be limited to any particular particle formation or deposition mechanism.

As noted previously, CO<sub>2</sub> cleaning procedures have traditionally been used in combination with a preliminary cleaning step such as bead-blasting. The combination of bead-blasting and CO<sub>2</sub> cleaning has generally not been used on virgin workpieces, but rather, has been employed on used workpieces that have had CVD coatings deposited on their surfaces during semiconductor processing. While this method has been found to be satisfactory for the removal of particulate contaminants, it lacks the ability to remove metallic contamination that occurs on both virgin and used workpieces.

The present invention recognizes that until the workpiece, be it a virgin component or a chemically-stripped component, is subjected to a final CO<sub>2</sub> cleaning step, problematic submicron particles which need to be eliminated from the surface of the components will remain. The need for removal of such particulate contaminants, as well as the manner in which such removal is achieved is neither appreciated nor performed in conventional processes.

Moreover, it appears that products resulting from the inventive process also possess superior levels of metallic purity as compared to re-worked products processed by cleaning methods which use CO<sub>2</sub> cleaning to clean the used coated workpieces. As noted above, one conventional process mechanically strips the coating from a used component, such as a boat, via bead blasting, and then uses CO<sub>2</sub> cleaning to complete the cleaning. Without wishing to be tied to any particular theory, in the case of a used boat, the conventional understanding is that surface metallic contamination is not a problem. Conversely, even if surface metallic contamination did give rise to problems, it was wrongly assumed that such problems could be sufficiently eliminated using techniques known in the prior art.

In contrast, some evidence suggests that a bead blasting step actually acts to increase the concentration of metallic impurities at the surface of the workpiece. This undesirable effect may be the result of the use of impure blasting media.

WO 02/09161

PCT/US01/23047

The process of the present invention is superior to the conventional bead blasting/ $\text{CO}_2$  cleaning process in that it does not result in metallic contamination of the surface of the stripped workpiece. In fact, the present inventive process acts to reduce the concentration of metals at the surface.

5

Likewise, for a virgin workpiece, such as an unused SiC boat, the conventional understanding of surface metallic impurity has been that  $\text{HF}$  or hot  $\text{HCl}$  cleaning offered only marginal utility because it served only to incrementally reduce the concentration of metals at the surface of the component to a level slightly below that of the bulk material forming the

10 workpiece (1-10 ppm for SiC), and that this relative purity advantage over the bulk disappeared over time as subsequent use under high temperature environments promoted the diffusion of bulk metals into the surface region of the component. Accordingly, the art did not require chemical stripping in all circumstances.

15 The surface of materials representing virgin SiC components has been analyzed by one conventional method (x-ray photoelectron spectroscopy, referred to herein as XPS) and by another method (secondary ion mass spectroscopy, referred to herein as SIMS). A conventional XPS analysis provides information at a depth of about 3 nm and has a sensitivity of about 0.1-1.0% depending upon the element of interest. In contrast, the SIMS analysis can

20 provide information at a depth of about 10 nm and has a sensitivity of about 0.2-3.0 ppm. For this reason, the SIMS test provides a more accurate method for measuring the surface concentration of metals in semiconductor processing components. It has been found that in instances where XPS failed to detect any metals, (and thus failed to provide any indication of an elevated surface metals concentration), the SIMS test reported about 2000 ppm metals at a

25 depth of 10 nm. In the field of high temperature semiconductor processing, these surface levels are clearly undesirable. Accordingly, as a result of the SIMS analysis, there is now a demonstrated need to clean the surface of a virgin ceramic component, preferably using a chemical stripping step, in order to reduce the high surface level of metallic contaminants present at the surface of semiconductor processing components. It should be appreciated that,

WO 02/09161

PCT/US01/23047

in one embodiment of the present invention, the surface is a CVD surface, which optionally may have been subjected to machining or other post-processing steps.

As outlined above, the chemical stripping step can employ a wide variety of chemical stripping agents. In particular, it may be a solvent having at least 1 v/o of an acid selected from the group consisting of HF, acids having a pKa of less than about one, and mixtures thereof. In one preferred embodiment, the chemical stripping agent is selected from the class of chlorinated acids. In particular, a chlorinated acid such as HCl can be used. Although HCl is desirable due to its high level of dissociation, other acid chlorides, including but not limited to chloroacetic acid, chloropropionic acid and chlorobenzoic acid may also be used. In one preferred embodiment, the chemical stripping step is carried out at elevated temperatures, i.e., about 85°C and above, as such temperatures have been found to result in improved surface purity.

As also noted, chemical stripping may be carried out using gas-phase chemical stripping agents. Exemplary gas-phase chemical stripping agents include halogen gasses and gasses containing halogenated compounds. Thus, chemical stripping may be achieved using gas phase chlorine, fluorine, bromine, iodine, etc., or gas-phase chlorinated compounds such as SiCl<sub>4</sub>. Gas-phase halogenated organic compounds may be used as well. As noted previously, these include, but are not limited to 1,1,1-trichloroethane (TCA) and 1,2-trans-dichloroethylene (DCE).

More particularly, it should be understood that the process of the present invention is intended to be applied to a wide variety of inorganic surfaces employed by semiconductor processing components. Such surfaces typically comprise ceramic materials such as those ceramics commonly used in semiconductor fabrication, however, the process may be applied to non-ceramic surfaces such as silicon and diamond as well. Thus, while the discussion has focused primarily on semiconductor processing components such as ceramic boats, and particularly those formed of SiC, it should be understood that the invention is not intended to

be limited in this manner. Rather, the invention is intended to apply to any of the semiconductor processing components that have inorganic surfaces associated with semiconductor wafer processing techniques. These surfaces include, but are not limited to silicon (Si), silicon carbide (SiC), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), diamond, yttria (Y<sub>2</sub>O<sub>3</sub>), zirconia (ZrO<sub>2</sub>), aluminum nitride (AlN), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), graphite and polycrystalline or fused quartz.

The surfaces may be vapor-deposited, and as discussed above may be deposited using CVD techniques. Such surfaces include, but are not limited to polycrystalline or other CVD Si, CVD SiC, CVD SiO<sub>2</sub>, CVD Si<sub>3</sub>N<sub>4</sub> and CVD diamond surfaces. Of course, it should be understood that despite the applicability of the present invention to surfaces having inorganic coatings thereon, the process may also be applied to uncoated, inorganic surfaces.

In considering SiC workpieces, several varieties are used in the art. In one embodiment, a workpiece formed simply of SiC is used. In another embodiment, the workpiece comprises a reduced porosity SiC formed by loading the pores of a SiC structure with Si. Because the silicon tends to escape from the pores, such workpieces are often provided with a CVD SiC layer. More specifically, these components typically are formed of a porous  $\alpha$ -SiC body having Si occupying the pores. To prevent the Si from escaping, a layer of very pure  $\beta$ -SiC is deposited on the surface of the component using CVD methods. The  $\beta$ -SiC is intended to seal the surface and inhibit loss of Si near the surface of the workpiece.

It should be understood that the  $\beta$ -SiC material deposited on the workpiece to prevent Si from escaping is not intended to be removed by the process of the present invention. Rather, when referring herein to the removal of coatings from used workpieces, the subject coatings are those that have been deposited on the workpiece during its use in semiconductor processing. Thus, a virgin coated workpiece refers to a newly manufactured workpiece having a desired coating formed thereon, while a used, coated workpiece refers to a workpiece having an undesired coating deposited during semiconductor processing. Of course, upon use, the

WO 02/09161

PCT/US01/23047

virgin coated workpiece acquires an additional, undesired coating, and it is the removal of the coating which forms one embodiment of the present invention.

While useful with vertical racks, it should be understood that the process of the present invention employing a strong acid clean followed by a CO<sub>2</sub> clean provides unexpected benefits not only for vertical racks, but also for semiconductor processing equipment of any shape. Examples of semiconductor processing components used in single wafer processing to which the present invention may be applied include, but are not limited to, bell jars, electrostatic chucks, focus rings, shadow rings, chambers, susceptors, lift pins, domes, end effectors, liners, supports, injector ports, manometer ports, wafer insert passages, screen plates, heaters, and vacuum chucks. Examples of semiconductor processing components used in batch processing to which the present invention may be applied include, but are not limited to, paddles, process tubes, wafer boats, liners, pedestals, long boats, and dummy wafers. Examples of semiconductor processing components used in chemical mechanical polishing (CMP) to which the present invention may be applied include, but are not limited to, conditioning pads and wafer holders.

Lastly, it is believed that the process of the present invention provides for the first time a ready-to-install product, that is, a product that can be safely taken out of a protective shipping bag at the user's facility and directly installed in a semiconductor furnace without any further cleaning by the user. This is achievable because such components already have the lowest possible amounts of surface metals and particles achievable by surface treatments.

More particularly, in one aspect of the present invention, immediately upon completing the CO<sub>2</sub> cleaning step, the cleaned workpiece is installed either into a furnace used for processing semiconductor wafers, or into a bag used for the shipping and storage of cleaned semiconductor processing components. In the former process, the workpiece is transferred directly from CO<sub>2</sub> cleaning into the furnace without any further cleaning steps. In the latter process, the workpiece is packaged, i.e., placed into a sealable container such as a bag and

sealed, directly following CO<sub>2</sub> cleaning without any further cleaning steps. In this latter case, upon removing the workpiece from its packaging, it is installed directly into a furnace used for processing semiconductor wafers without any further cleaning steps. Unlike processes known in the art in which it is necessary to provide additional cleaning steps between removal of the workpiece from its packaging and installation in the furnace, components cleaned using the method of the present invention may be installed into the furnace immediately upon removal from their packaging. This is advantageous in that it eliminates additional processing steps which can, among other things, actually lead to increased levels of contamination, particularly particulate contamination.

10

In certain circumstances, those using the cleaned components of the present invention have a need to provide additional surface coatings on a workpiece prior to installing it in semiconductor processing equipment. For example, it may be desirable to deposit a polysilicon layer, a silicon oxide layer, a silicon nitride layer, a metallic layer, a photoresist layer or some other layer upon the workpiece prior to using that workpiece in a semiconductor fabrication process. Typically, the semiconductor manufacturer must deposit or otherwise lay down that layer upon the workpiece once it has been removed from any packaging. This process, however, has the potential of introducing contaminants to the workpiece surface. The present invention, however, eliminates this problem by allowing the workpiece to have one or more desired layers provided on its surface immediately after the cleaning process has been carried out, and immediately before packaging the workpiece for shipping or storage. Thus, the present invention contemplates a process in which, upon completion of the CO<sub>2</sub> step, one or more coating layers are provided onto the workpiece surface. Optionally, once said one or more additional coating layers have been provided on the workpiece, a second cleaning employing a chemical stripping step and a CO<sub>2</sub> step, of the types described above may be applied to the coated workpiece prior to packaging.

25

In certain circumstances, such as when using virgin workpieces, removal of particulate contaminants may not be needed. Thus, in a further embodiment of the invention, the

WO 02/09161

PCT/US01/23047

workpiece is chemically stripped as described above, provided with an additional surface coating such as a polysilicon layer, a silicon oxide layer, a silicon nitride layer, a metallic layer, a photoresist layer, or some other layer, and then either packaged or placed directly in semiconductor processing equipment for immediate use. This embodiment offers the advantage of providing a cleaned, coated workpiece that can be used immediately upon removal from its packaging without the need for additional cleaning or coating steps in the semiconductor processing equipment.

Purity may be further enhanced by performing any or all of the processing steps in a clean-room environment. Thus, the workpiece may be processed entirely in a clean-room environment from the initial chemical stripping step, or it may be moved to such an environment prior to the CO<sub>2</sub> step, the optional coating step, the optional final chemical stripping step, or the optional CO<sub>2</sub> step.

Although several prior art cleaning regimes, and their advantages and disadvantages, have been described previously herein, none of those known in the art offer the ability to provide a surface having the low contamination level of metallics and particles available from the inventive process described herein. Simply washing in a strong acid solution, such as a solution containing HF or other acid having a pKa of less than about one, provides a surface having unsatisfactory levels of particulate contaminants. Alternatively, simply washing in a weak acid solution or bead-blasting followed by a CO<sub>2</sub> cleaning results in less desirable levels of metallic contaminants. It was not until the present invention, in which chemical stripping is followed by CO<sub>2</sub> cleaning, that one could achieve acceptable levels of both metallic and particulate contamination.

25

In another embodiment of the present invention, the chemical stripping and CO<sub>2</sub> cleaning steps are coupled with a modified high-purity bead blasting step. Specifically, in this embodiment, the invention includes the steps of bead-blasting the surface of the workpiece using green SiC particles. Subsequently, the surface is contacted with a solvent having at



WO 02/09161

PCT/US01/23047

least 1 v/o of an acid selected from the group consisting of HF, acids having a pKa of less than about one, and mixtures thereof. The surface is then treated using CO<sub>2</sub> cleaning. The use of green SiC in the bead-blasting step is unique in that, to date, only black SiC has been used for bead-blasting purposes. In the present invention it has been found that bead-blasting using green SiC beads provides surfaces that are significantly lower in contaminants. This is believed to be the result of the composition of the black SiC beads versus the green SiC beads. Whereas the former comprise a grit containing about 98% SiC, (and an impurity level of about 2%), the latter contain impurities in the range of approximately 1000-2000 parts per million, (i.e., 0.1-0.2% impurities).

10

In still another embodiment of the present invention, the chemical stripping step can be eliminated entirely and replaced with a bead blasting step using green SiC beads described above. Thus, the process employs the steps of bead-blasting with green SiC followed by a CO<sub>2</sub> cleaning.

15

In yet another embodiment, the use of a chemical stripping step can be eliminated when cleaning certain components. Specifically, as noted above, certain workpieces may be provided with coatings. Such coatings may be provided by any of a wide variety of processes including chemical vapor deposition, sputter deposition and spray coating. For example, a workpiece formed of  $\alpha$ -SiC may be provided with a CVD deposited  $\beta$ -SiC coating to form a very pure surface. Likewise, thick CVD deposited SiC films of up to about 500 microns in thickness usually do not require additional machining steps, and thus avoid one significant source of metallic contamination. Alternatively, workpieces formed from other ceramic materials may be such that they do not require certain processing steps, such as sandblasting, that introduce metallic impurities onto the ceramic surface. These workpieces also have surfaces that are low in metallic contaminants. New workpieces having such coated or otherwise pure surfaces are relatively free of metallic contaminants. Of course, any of the surfaces described above will include some low level of unavoidable metallic impurities, however, such impurity levels are significantly lower than those introduced by machining

25

steps such as sandblasting. As such, these workpieces can be cleaned using only the CO<sub>2</sub> process and installed directly into a furnace or immediately packaged without any additional cleaning steps. Likewise, the packaged workpieces of this type can be removed from their packaging and directly installed into a furnace without any additional cleaning steps. Thus, although the prior art includes processes in which the CO<sub>2</sub> process is used without a chemical stripping step, none of these processes are used in connection with virgin workpieces of the type described above. By eliminating the chemical stripping step for certain virgin workpieces, cleaning time and process complexity can be minimized.

It is noted that in each of the embodiments employing green SiC described above, the CO<sub>2</sub> cleaning step may employ techniques and apparatus that are known in the art. One example of a satisfactory CO<sub>2</sub> method and delivery system is that described in U.S. Patent Application Serial Number 08/890,116, entitled "Carbon Dioxide Cleaning Process", the teachings of which are incorporated herein by reference.

Further improvements include the use of high purity CO<sub>2</sub> in the CO<sub>2</sub> cleaning step and the application of the present process, to the extent possible, in a clean-room environment. Needless to say, any reduction in impurities in the environment surrounding the workpiece during or after cleaning will result, ultimately, in a cleaner workpiece.

20

#### Examples

Results are presented below for several tests of the steps used in the inventive process. In Table 1, CVD SiC coated parts that had been subjected to machining (i.e., wet or dry sandblasting) were analyzed for metallic impurities. These samples were measured either directly after the sandblasting, after a post-sandblasting weak acid treatment, or after the samples had been subjected to the inventive process (HF/CO<sub>2</sub>) post-sandblasting. The ability of the inventive process to provide improved metal removal, particularly for iron can be seen in the Table.

WO 02/09161

PCT/US01/23047

**TABLE 1 - Metallic Impurities in Parts Per Million**

PROCESS	Na	Al	Ti	V	Cr	Fe	Ni
WS	6	54	3	0.5	14	115	2
WS weak acid	6	33	1	0.1	8	38	0.8
WS Invention	2	17	1	0.05	6	28	2
DS	136	98	60	10	4	1441	18
DS weak acid	132	60	39	7	3	381	8
DS Invention	7	107	20	3	4	211	4

WS -- Wet Sandblast

DS -- Dry Sandblast

Results from SIMS approximately 10 nm below surface.

5

Table 2 presents particulate impurity data for non-machined samples that do not have CVD coated surfaces. Samples 1-6 were treated with conventional workpiece cleaning steps, and samples 7-10 were cleaned using the process of the present invention. The numbers of particulate impurities are presented for two sides of each sample.

10

WO 02/09161

PCT/US01/23047

**TABLE 2 - Particulate Impurities I**

Sample	Process	Side 1	Side 2
1	Conventional	0.98	1.12
2	Conventional	0.8	0.67
3	Conventional	0.77	0.78
4	Conventional	0.99	0.86
5	Conventional	1.34	1.23
6	Conventional	0.79	0.86
7	CO <sub>2</sub>	0.03	0.17
8	CO <sub>2</sub>	0.14	0.12
9	CO <sub>2</sub>	0.05	0.03
10	CO <sub>2</sub>	0.04	0.12

Table 3 presents particulate impurity data for samples before and after treatment with the CO<sub>2</sub> process described above. In samples A, B and C, the sample is machined SiC that does not have a CVD coating on its surface. Sample D is a non-machined sample having a CVD SiC surface. As can be seen, the use of the CO<sub>2</sub> process significantly reduces the amount of particulate contaminants.

**TABLE 3 - Particulate Impurities II**

Sample	Particles Before	Particles After
A	0.35	0.04
B	0.54	0.13
C	0.55	0.09
D	0.65	0.01

10

Equivalents

From the foregoing detailed description of the specific embodiments of the invention, it

WO 02/09161

PCT/US01/23047

should be apparent that a novel system for removing metallic and particulate contaminants from ceramic workpieces has been described. Although particular embodiments have been disclosed herein in detail, this has been done by way of example for purposes of illustration only, and is not intended to be limiting with respect to the scope of the appended claims

5 which follow. In particular, it is contemplated by the inventors that various substitutions, alterations, and modifications may be made to the invention without departing from the spirit and scope of the invention as defined by the claims.

WO 02/09161

PCT/US01/23047

# CLAIMS

We Claim:

1. A process for cleaning a semiconductor processing component having an inorganic surface,  
5 the process comprising the steps of:
  - a) exposing the inorganic surface to a chemical stripping agent selected from a group that excludes an agent consisting of hydrofluoric acid, and
  - b) directing a flow of frozen CO<sub>2</sub> pellets upon the surface.
- 10 2. The process of claim 1, wherein the chemical stripping agent comprises a chlorinated acid.
3. The process of claim 2, wherein the chlorinated acid is selected from the group consisting of HCl, chloroacetic acid, chloropropanic acid, chlorobenzoic acid, and mixtures thereof.
- 15 4. The process of claim 1, wherein the chemical stripping agent comprises a gas phase chemical stripping agent.
5. The process of claim 4, wherein the chemical stripping agent comprises a halogen or  
20 halogenated compound.
6. The process of claim 5, wherein the halogen is selected from the group consisting of chlorine, fluorine, bromine and iodine.
- 25 7. The process of claim 5, wherein the halogenated compound comprises SiCl<sub>4</sub>.
8. The process of claim 5, wherein the halogenated compound is a halogenated organic compound.

9. The process of claim 8, wherein the halogenated organic compound is selected from the group consisting of 1,1,1-trichloroethane, 1,2-trans-dichloroethylene and mixtures thereof.
10. The process of claim 1, wherein the chemical stripping step is carried out at a temperature  
5 above room temperature.
11. The process of claim 10, wherein the chemical stripping step is carried out at a temperature of at least about 85°C.
- 10 12. The process of claim 1, wherein the surface is exposed to the chemical stripping agent for a time sufficient to provide the surface with a metallic contaminant concentration of at most about 600 ppm, as measured by SIMS at a depth of about 10 nm.
13. The process of claim 1, wherein the surface is exposed to the chemical stripping agent for  
15 a time sufficient to provide a surface concentration of metal contaminants other than alkaline and alkaline earth metals of at most about 400 ppm, as measured by SIMS at a depth of about 10 nm.
14. The process of claim 1, wherein the surface is exposed to the chemical stripping agent for  
20 a time sufficient to provide the surface with an iron contaminant concentration of at most about 225 ppm, as measured by SIMS at a depth of about 10 nm.
15. The process of claim 1, wherein the chemical stripping agent comprises a supercritical fluid.  
25
16. The process of claim 1, wherein the surface is exposed to the flow of frozen CO<sub>2</sub> pellets for a time sufficient to provide a surface particulate contamination of at most about 0.4 particles larger than about 0.3 µm per square centimeter.

WO 02/09161

PCT/US01/23047

17. The process of claim 1, wherein after the flow of frozen CO<sub>2</sub> pellets is directed onto the surface, the component is installed in a furnace used for processing semiconductor wafers.
18. The process of claim 17, wherein no additional cleaning steps are carried out between  
5 completing the flow of frozen CO<sub>2</sub> pellets and installing the component in the furnace.
19. The process of claim 17, wherein after completing the flow of frozen CO<sub>2</sub> pellets and prior to installing the component in the furnace, at least one additional material layer is deposited on the surface.  
10
20. The process of claim 19, wherein said at least one additional material layer comprises a polysilicon layer, a silicon oxide layer, a silicon nitride layer, a metallic layer, a photoresist layer, and combinations thereof.
- 15 21. The process of claim 19, wherein after said at least one additional material layer is deposited on the surface, the deposited layer is subjected to a process comprising the steps of:
- a) exposing said at least one additional material layer to a chemical stripping agent,  
and  
20 b) directing a flow of frozen CO<sub>2</sub> pellets upon the surface.
22. The process of claim 1, wherein after the flow of frozen CO<sub>2</sub> pellets is directed onto the surface, the component is sealed in a package suitable for storage and transport.
- 25 23. The process of claim 22, wherein no additional cleaning steps are carried out between completing the flow of frozen CO<sub>2</sub> pellets and packaging the component.



24. The process of claim 22, wherein after completing the flow of frozen CO<sub>2</sub> pellets and prior to packaging the component, at least one additional material layer is deposited on the surface.
- 5 25. The process of claim 24, wherein said at least one additional material layer comprises a polysilicon layer, a silicon oxide layer, a silicon nitride layer, a metallic layer, a photoresist layer, and combinations thereof.
26. The process of claim 24, wherein after said at least one additional material layer is  
10 deposited on the surface, the deposited layer is subjected to a process comprising the steps of:  
a) exposing said at least one additional material layer to a chemical stripping agent,  
and  
b) directing a flow of frozen CO<sub>2</sub> pellets upon the surface  
15
27. The process of claim 22 which includes the further steps of removing the component from the package and installing the component into a furnace used for processing semiconductor wafers.
- 20 28. The process of claim 27 wherein no additional cleaning steps are carried out between removing the component from the package and installing it into the furnace.
29. The process of claim 1, wherein prior to the step of exposing the inorganic surface to the chemical stripping agent, the component is subjected to blasting with green SiC.  
25
30. The process of claim 1, wherein the inorganic surface is selected from the group consisting of Si, diamond, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, AlN, Al<sub>2</sub>O<sub>3</sub> and polycrystalline or fused quartz.

31. The process of claim 1, wherein the inorganic surface has a vapor-deposited coating thereon.
32. The process of claim 31, wherein the vapor-deposited surface is a vapor-deposited material selected from the group consisting of CVD Si, CVD SiO<sub>2</sub>, CVD SiC, CVD Si<sub>3</sub>N<sub>4</sub>, CVD diamond, Y<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.
33. The process of claim 1, wherein the inorganic surface comprises a coating provided by sputter deposition or spray coating.
34. The process of claim 19, wherein after providing said at least one additional material layer, no additional cleaning steps are carried out before the component is installed in a furnace used for processing semiconductor wafers.
35. The process of claim 19, wherein after providing said at least one additional material layer, and prior to installing the component in a furnace used for processing semiconductor wafers, the product is sealed in a package suitable for storage and transport.
36. The process of claim 35, wherein no additional cleaning steps are carried out between providing said at least one additional material layer and packaging the component.
37. A process for cleaning a semiconductor processing component having an inorganic surface, the process comprising the steps of:
- a) exposing the inorganic surface to a chemical stripping agent selected from a group that excludes an agent consisting of hydrofluoric acid,
  - b) directing a flow of frozen CO<sub>2</sub> pellets upon the surface, and
  - c) depositing at least one additional material layer on the surface.

38. The process of claim 35 wherein no additional cleaning steps are carried out between removing the component from the package and installing it into the furnace
39. A process for cleaning a semiconductor processing component having an inorganic  
5 surface, the process comprising the steps of:
- a) exposing the inorganic surface to a chemical stripping agent, and
  - b) exposing the surface to sonic energy.
40. A process for cleaning a semiconductor processing component having an inorganic  
10 surface, the process comprising the steps of:
- a) exposing the inorganic surface to a chemical stripping agent,
  - b) depositing at least one additional material layer on the surface, and
  - c) sealing the workpiece in a package suitable for storage and transport.
41. The process of claim 40, wherein no additional cleaning steps are carried out between  
15 depositing the at least one additional material layer and packaging the workpiece.
42. A process for cleaning a semiconductor processing component having an inorganic  
surface, the process comprising the steps of:
- 20
- a) exposing the inorganic surface to a chemical stripping agent,
  - b) depositing at least one additional material layer on the surface, and
  - c) installing the workpiece in a furnace used for processing semiconductor wafers.
43. The process of claim 42, wherein no additional cleaning steps are carried out between  
25 depositing the at least one additional material layer and installing the workpiece in the furnace.

WO 02/09161

PCT/US01/23047

44. The process of claim 42, wherein after providing said at least one additional material layer, and prior to installing the component in a furnace used for processing semiconductor wafers, the product is sealed in a package suitable for storage and transport.

- 5 45. The process of claim 44, wherein no additional cleaning steps are carried out between providing said at least one additional material layer and packaging the component.

10